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THE SPECTRUM OF SHOCK-HEATED GASES
SIMULATING THE VENUS ATMOSPHERE

by

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The Spectrum of Shock-Heated Gases Simulating the Venus Atmosphere

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ABSTRACT

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Mixtures of 90% N_2 plus 10% CO_2 , and 80% N_2 plus 20% CO_2 have been heated by reflected shock waves to temperatures of about 8000°K and normal density. Photographic and photo-electric measurements have been made of the emitted radiation in the region 0.23 μ to 1.2 μ . The CN radical is the most prominent radiator in these experiments and the intensity of the emission may be used to derive transition probabilities for the violet and red systems of bands.

AUTHOR



INTRODUCTION

The composition of the atmosphere of Venus is not known with any certainty. The spectrum of Venus shows some strong bands in the photographic infrared which may certainly be attributed to carbon dioxide but to date no other constituent of the atmosphere has been identified. Early estimates of the composition (see Ref. 1) tended to favor a predominance of CO_2 , about 85 parts per cent, with N_2 and a little oxygen making up the remainder. Lately the estimates have been revised and atmospheres with a preponderance of N_2 have been suggested.²

While the estimate must remain somewhat arbitrary, it is clear that the atmosphere of Venus does differ from that of the Earth by the inclusion of an appreciable proportion of CO_2 . Thus it is to be expected that the equilibrium composition of the atmosphere heated to high temperatures, as for example at the gas cap of an incoming vehicle will contain the decomposition products of CO_2 plus cross-products with nitrogen.

These new constituents may well modify the radiation pattern as compared with that of hot air and the present investigation has been made to study this effect.

EXPERIMENTAL

The gas has been heated in a shock tube, 10 feet long and 1 1/2 inches in diameter. The driver is some two feet long and either cold hydrogen or combustion drive may be used. For combustion drive, stoichiometric mixtures of oxygen and hydrogen diluted with about 4 parts of helium are used, the mixture being ignited by an exploding wire strung down the length of the driver.

Shock speeds are measured by the time interval between signals from ionization pick-ups at stations down the tube. Typical experimental conditions have been an initial charging of the tube to a pressure of 10mm Hg with experimental gas, a diaphragm bursting at around 2000 psi. Shock speeds of around 4.5mm/ μ sec are achieved. The initial gas mixture was made up by partial pressures in a mixing tank and left overnight before use. Commercial nitrogen and carbon dioxide were mixed without purification to give 20% CO₂, 80% N₂, and 10% CO₂, 90% N₂. The shock tube could be evacuated to pressures has been 1 μ Hg and with leak rates of about 1 μ Hg per minute accidental modification of the initial gas composition was not important.

The tube was closed by an end plate with a flush mounted window in its center and observations were made on the gas processed by the reflection of the incident shock from the end wall. The gas was thus viewed axially down the tube.

With this arrangement, there were about 30 μ s between the reflection of the shock and the interaction of the reflected shock with the boundary layer and the contaminated region in front of the driver which causes a heavy masking of the spectrum with impurities and an effective end of the experiment. An extensive account of properties of reflected shocks is given in Ref. 3.

Preliminary observations of the spectrum were made with a medium quartz spectrograph fitted with a drum camera. The slit of the spectrograph was lined up close to the window and no lens was used. With a slit height of about 1mm and the 12 inch circumference drum spinning at 400 rps, a time resolution of about 10 μ s could be obtained. With a 50 μ entrance slit width, single shot spectra could be obtained.

The entire photographic region between the limit of Kodak IN film at 0.9μ and the violet limit of 103-0 film at 0.23μ was examined.

The drum camera observations gave valuable qualitative measures of the spectrum and these were followed up by quantitative measurements made with a photo-electric scanning spectrometer. This instrument was built by J. C. Camm of this laboratory and will be fully described elsewhere. It has a dispersion of about 300\AA per mm and can scan about 30\AA per μ sec. Thus, it could scan about 900\AA per experiment. With blue and red sensitive photomultipliers the region between 1.2μ and 0.3μ has been investigated. Order sorting was done with Corning filters.

The photomultipliers were calibrated against sub-standard tungsten lamps and the emissivity curves for tungsten given by DeVos⁴ were used together with black body tables to make the calibration absolute.

A portion of the radiation entering the spectrometer was monitored by a second photomultiplier to show when the experiment was over and as an overall check on the reproducibility. In general the observed radiation could be reproduced to better than $\pm 50\%$.

RESULTS

The photographic records obtained showed that the radiation from the CN radial was by far the biggest factor with the mixtures and conditions already described. Both the red, $A^2\pi \rightarrow X^2\Sigma$, and violet, $B^2\Sigma \rightarrow X^2\Sigma$, transitions were observed. The red system extends from about 2μ down to about 0.4μ with its main strength lying in the region 1.2μ to 0.6μ . The CN violet system is mainly confined to the (0, 2) (0, 1) (0, 0) and (1, 0) sequences, a few of the tail bands were identified but their contribution to the spectrum was very small. None of the other CN

systems⁵ was identified.

Besides the carbon line at 2478\AA , the only other carbon containing species observed was the C_2 Swan band system - but this was fairly weak. The carbon monoxide 4th positive system which might be expected to radiate at about 2500\AA and was not observed.

The other spectral features noted in this survey included the N_2 1st positive and N_2 2nd positive and a continuum extending from the blue to beyond 2500\AA . The source of this continuum has yet to be identified.

The signals from the photo-electric scanner were recorded from an oscillograph trace, Fig. 1. The true emission record was distorted since both the wavelength and depth of hot gas were changing at the same time. All the recorded intensities was scaled to a time corresponding with a depth of 1 cm of radiating gas, using a computed value for the reflected shock speed. The simple assumption was made that the gas was optically thin and thus the radiation was proportional to the depth. In some of the records obtained for the CN violet this was clearly untenable (Fig. 1(b)), but in the red the assumption is justifiable. As a check, a few runs were made with the scanner immobile and the spectrometer set at a wavelength of 9225\AA with the aid of an argon discharge (Fig. 1(a)). The emission at this wavelength is quite intense but the records showed a fairly linear rise with time. Although the rise may appear linear, over a small distance, self-absorption can still be causing a lower level to be recorded.

The scanner also recorded some atomic lines which were not seen on the films, these were oxygen and nitrogen lines and although the peak intensities were high, their width was narrow and the total radiation was small compared with the band spectrum.

GAS PROPERTIES

The equilibrium gas temperature, density and compositions were calculated from a machine program supplied by Los Alamos Scientific Laboratory. Both the incident and reflected shock conditions were calculated. This program uses input data from the JANAF⁶ Tables which do not extend above 6000°K.

The calculations were made up to temperatures of about 8000°K and so must be regarded as approximate. Ionization was not taken into account. Since the CN radical was the main radiator its concentration was of most interest. It is unfortunate that there is considerable doubt about its dissociation energy. The JANAF Tables use a value of H_0^0 corresponding with a dissociation energy of 8.35ev while other authors,⁷ have given arguments for 8.2ev, and yet others⁸ have given 7.6ev. At the temperature and pressures of these experiments there is roughly a factor of two between the computed CN concentration using $D_0 = 7.6\text{ev}$ and $D_0 = 8.35\text{ev}$. There is also a neglect in the input data of higher excited states of CN, which will be significantly populated in the experiments.

INTENSITY OF RADIATION

The CN red system is the $A^2\pi \rightarrow X^2\Sigma$ transition of the molecule and will thus have 12 rotational branches. Each vibrational level will thus be split into a large number of sub-levels and these cover the region between vibrational levels, resulting in a fairly continuous coverage of the spectrum. Self-absorption only becomes serious when the intensity at a particular wavelength approaches the black body limit and a smearing of the transition over a large wavelength interval tends to keep the spectral intensity low. Since the resolution in these experiments was

much too low to see details of the rotational spectrum we shall here consider only the integrated intensities of the various vibrational transitions. A listing⁹ of the band heads shows the transition extending from 4400\AA to beyond $14,000\text{\AA}$ but the investigation here shows the region below 5700\AA to be unimportant. Dixon and Nicholls¹⁰ have made an investigation of the relative intensities in the system and their values may be coupled with the relative populations of the vibrational levels to calculate the contributions of each band to the total: The results show that at 8000°K only about 10% of the total band intensity lies in the region beyond 1.2μ which could not be recorded. Only about 2% lies in the blue region beyond 0.58μ .

The emission intensity of a radiator may simply be written as $I_{\text{em}} = N h \nu A$ where N is the number of emitters; h is Planck's constant; A is the Einstein spontaneous emission probability; and ν is the frequency of the radiation. A is proportional to the quantum mechanical electronic transition probability R_e^2 and also to ν^3 . Normally, R_e is a function of the internuclear separation and thus varies from band to band. In the case of CN red Dixon and Nicholls¹⁰ have shown this variation to be small. Thus A will be a meaningful parameter for the whole band system.

The proportionality of the intensity of radiation with number of emitted assumes that once emitted radiation will not be re-absorbed. Now in general, the radiation emitted will be given by $I_\nu = B_B(1 - \exp(-\alpha_\nu x))$ where B_B is the black body function; α_ν is the absorption coefficient at ν and x is the depth of radiating gas. When $\alpha_\nu x$ is small $I_\nu = B_B \alpha_\nu$ and is proportional to the number of molecules in the ground state. The quantity $(1 - \exp(-\alpha_\nu x))$ is the emissivity ϵ , of the gas sample. Thus, if a given measured intensity is corrected by the factor

$a_{\nu} = \exp(-a_{\nu} x) \equiv -\epsilon^{-1} \ln(1 - \epsilon)$, the effect of self-absorption will be allowed for. Strictly, the relations given only apply to monochromatic light since a is a rapidly varying function of ν . As already noted, the condition of high pressure and temperature in these experiments, together with the characteristics of a molecular emission tend to smear the detailed structure expected at low temperature and pressures and we shall be approximately justified in treating the band as having an average absorption coefficient. A more refined correction will require a detailed knowledge of the line shapes which can be obtained from a study under high dispersion.

Another correction to be made concerns the effect of induced emission. When the population of the upper state becomes appreciable compared with the ground state induced emission will cause the apparent transition probability to exceed the true value by the factor¹¹
 $(1 - \exp(-h c / \lambda kT))^{-1}$

In Fig. 2 is given the observed intensity of the CN red system. By comparison with the black body curve it can be seen that the average emissivity of the gas is about 0.25 and the self-absorption correction will be about 1.16, the induced emission factor is $(1 - \exp(-1.44 / 0.9 \times 10^{-5} \times 8000))^{-1} = 1.16$. These two factors then cancel out.

Now the integrated radiation under the curve is $530 \text{ watts cm}^{-3} \text{ steradian}^{-1}$ with a median wavelength of 0.9μ . The computed value for the total number of CN radicals under these conditions is $6.6 \times 10^{17} \text{ per cm}^3$ if $D_0 \approx 8.35 \text{ ev}$ and $3 \times 10^{17} \text{ per cm}^3$ if $D_0 = 7.6 \text{ ev}$. The partition functions for the CN molecule have been given by Burhorn and Weinecke¹² and may be used to find the fraction of molecules in the $A^2 \pi$ state. As already stated, the radiation here observed represents about 90% of the

to transition. From the observed radiation a contribution must be subtracted to allow for the N_2 1st positive radiation which will be the only other main radiation. This may be estimated as $50 \text{ watts cm}^{-3} \text{ steradian}^{-1}$.¹³ Thus, we obtain $A = 1.4 \times 10^5 \text{ sec}^{-1}$ if $D_0 = 8.35 \text{ ev}$ and $A = 2.8 \times 10^5 \text{ sec}^{-1}$ if $D_0 = 7.6 \text{ ev}$.

VIOLET SYSTEM

In Fig. 3 is plotted the intensity in the violet obtained with a 10% CO_2 mixture. Figure 1(b) has shown strong self-absorption occurring in the (0,0) band, and although the intensity at 3900A, i.e., the (0,0) band is apparently of the same order as that at 4200A, i.e., the (0,1) band, this is a distortion. The emission at 4200 is not strongly self-absorbed and will be used to derive an approximate A value for the violet system. The Frank-Condon factors for this system have been given by Nicholls¹⁴ up to the third vibrational level. While this restricted array is insufficient for detailed calculation, it may be used to show that approximately 5% of the total transition lies in the (0,1) sequence of bands. Here we estimate the integrated emission to be about 20 watts. The computed density of CN is $3.6 \times 10^{17} \text{ per cm}^3$ and at the equilibrium temperature of 4600°K, 1 in 213 are in the $B^2\Sigma$ state we thus obtain $A = 6 \times 10^6 \text{ sec}^{-1}$ if $D_0 = 8.35 \text{ ev}$ and $A = 1.2 \times 10^7 \text{ sec}^{-1}$ for $D_0 = 7.6 \text{ ev}$. The results may be summarized:

TABLE I

System	Wavelength	$A \text{ sec}^{-1}$	
		$D_0 = 8.35 \text{ ev}$	$D_0 = 7.6 \text{ ev}$
Red	0.9μ	1.4×10^5	2.8×10^5
Violet	0.42μ	6×10^6	1.2×10^7

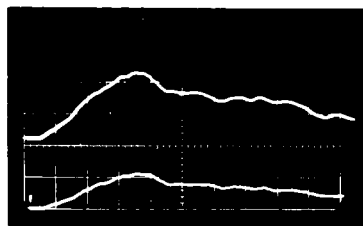
COMPARISON WITH OTHER WORK

Bennet and Dalby¹⁵ have given for the CN violet $A = 1.18 \times 10^4 \text{ sec}^{-1}$ at about 0.39μ , this may be scaled with the ν^3 dependence to give $0.9 \times 10^7 \text{ sec}^{-1}$ at 0.42μ . Tsang, Bauer and Cowperthwaite,⁷ have given f number estimates for the system of $1/2$ to $1/3$ of Bennet and Dalby's value. No direct values for the transition probability for the red system are known to the author although Herzberg and Phillips¹⁶ remark that the oscillator strengths of the red and violet systems are both apparently of the same order. Recently, Radford and Broida¹⁷ have found that the $\nu' = 10$ level of $A^2\pi$ has a radiative lifetime 6.7 times that of the $\nu' = 0$ level of $B^2\Sigma$. The $A^2\pi \nu' = 10$ level will have its main strength at about 0.55μ . Scaling the figures in Table I we obtain a ratio of 12. It must be stressed that this comparison is very approximate, but it does show at least order of magnitude agreement between the two sets of data.

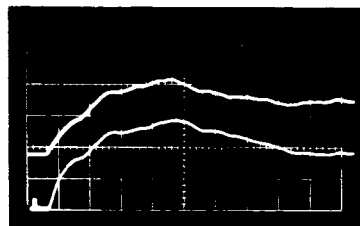
In conclusion we may note that if the results given here agree quite well with Bennet and Dalby's value if $D_0 \text{ CN} = 7.6 \text{ ev}$. On the other hand they agree better with Tsang et al if $D_0 \text{ CN} = 8.35$.

REFERENCES

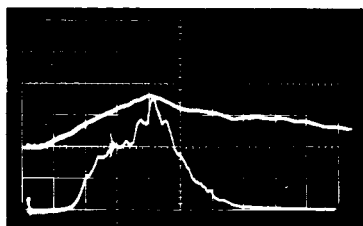
1. Lowe, R. E., Gervais, R. L., A.R.S.J., 32, 1660 (1962).
2. Coulson, K. L. and Lotman, M., "Molecular Optical Thickness of the Atmospheres of Mars and Venus," G.E. Report R625 D71 (1962).
3. Keck, J. C., Camm, J. C., Kivel, B., and Wentink, T., An. Phys., 7, 1 (1959).
4. DeVos, J. C., Physica, 20, 690 (1954).
5. Douglas, A. E. and Routly, P. M., Ap. J. Supp. 9, 1, 295 (1955).
6. JANAF Interim Thermochemical Tables (The Dow Chemical Company, Midland, Michigan 1960) Vol. 1.
7. Tsang, W., Bauer, S. H. and Cowperthwaite, M., J. Chem. Phys., 36, 1768 (1962).
8. Knight, H. T. and Rink, J. P., J. Chem. Phys., 35, 199 (1961).
9. Gaydon, A. G., and Pearse, R. W. B., Identification of Molecular Spectra, (Wiley, New York 1950).
10. Dixon, R. N. and Nicholls, R. W., Can J. Phys., 36, 127 (1958).
11. Mitchell, A. C. G. and Zemansky, M. W., Resonance Radiation and Excited Atoms. (C. U. P. 1961) p. 95.
12. Burhorn, F. and Wienecke, R., Z. Phys. Chem., 212, 105 (1959).
13. Kivel, B and Bailey, K., Tables of Radiation from High Temperature Air., Avco-Everett Research Laboratory Research Report 21 (1957).
14. Nicholls, R. W., Ap. J., 119, 286 (1959).
15. Bennet, R. G., and Dalby, F. W., J. Chem. Phys., 36, 399 (1962).
16. Hertzberg, G. and Phillips, J. G., Ap. J. 108, 163 (1948).
17. Radford, H. E. and Broida, H. P., J. Chem. Phys., 38, 644 (1963).



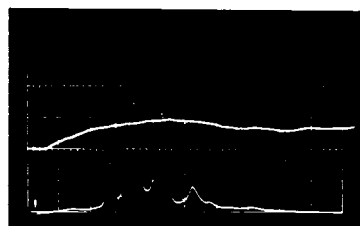
(a)



(b)



6632 → | ← 7091
6928 → |
λ →
(c)



3590 → | ← 4606
3883 → | ← 4216
λ →
(d)

LEGEND: UPPER TRACES MONITOR; TIME INCREASES TO RIGHT, $10\mu s$. PER DIVISION

(a) LOWER BEAM SET AT 9225 \AA , 20% CO_2 , 80% N_2 , $p_1 = 10\text{ mm Hg}$ $U_S = 4.4\text{ mm}/\mu s$.

(b) LOWER BEAM SET AT 3888 \AA , 10% CO_2 , 90% N_2 , $p_1 = 10\text{ mm Hg}$ $U_S = 4.2\text{ mm}/\mu s$.

(c) SCANNER GOING: 20% CO_2 , 80% N_2 , $p_1 = 10\text{ mm Hg}$ $U_S = 4.4\text{ mm}/\mu s$.

(d) SCANNER GOING: 10% CO_2 , 90% N_2 , $p_1 = 10\text{ mm Hg}$ $U_S = 4.3\text{ mm}/\mu s$.

Fig. 1 Oscillograms obtained with scanning spectrometer.